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(54) Title: TREATMENTS FOR INHIBITING VINYL AROMATIC MONOMER POLYMERIZATION

## (57) Abstract

Compositions and methods for inhibiting vinyl aromatic monomer polymerization during processing are disclosed. The compositions are combinations of a dinitrosalicylic acid derivative and a hydroxylamine compound and are added to the monomer during processing. The preferred composition is 3,5-dinitrosalicylic acid or 3,5-dinitrosalicylic methyl ester and bis-(hydroxypropyl)hydroxylamine in a weight ratio ranging from 1:9 to 9:1.

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## TREATMENTS FOR INHIBITING VINYL AROMATIC MONOMER POLYMERIZATION

### TECHNICAL FIELD

This invention relates to compositions and methods for inhibiting the unwanted polymerization of vinyl aromatic monomers during their processing.

### 5 BACKGROUND ART

Common industrial methods for producing vinyl aromatic monomers, such as styrene, typically include separation and purification processes such as distillation to remove unwanted impurities. Unfortunately, 10 purification processes carried out at elevated temperatures result in an increased rate of undesired polymerization. Distillation is generally carried out under vacuum to minimize loss of monomer. The presence of oxygen, although virtually excluded in styrene distillation, will also promote polymerization of the monomer.

U.S. Pat. No. 4,774,374, Abruscato et al., teaches compositions and processes for inhibiting the polymerization of a vinyl aromatic compound employing an oxygenated species formed by the reaction of oxygen and an N-aryl-N'-alkyl-p-phenylenediamine. U.S. Pat. No. 4,720,566,  
5 Martin, teaches methods and compositions for inhibiting polymerization of acrylonitrile in the quench tower, no oxygen excluded, using a hydroxylamine compound and a p-phenylenediamine compound.

Czechoslovakia Patent No. 163,428 teaches a method for stabiliz-  
10 ing styrene and divinylbenzene using 2,4-dinitroorthocresol and diethylhydroxylamine. European Patent Application 0 240297 also teaches the use of this combination to inhibit polymerization of styrene. Both these disclosures treat systems at lower temperatures and higher oxygen contents. The use of diethylhydroxylamine is problematic in styrene purification  
15 tion processes as it has a boiling point (125° to 130°C at 760 mm Hg) similar to that of styrene and can carry over with the styrene during purification processing.

A variety of inhibitor compositions have been employed in styrene  
20 and other vinyl aromatic monomers to inhibit undesirable polymerization. Amongst others, agents that have been used include sulfur, p-benzoquinone, phenylenediamine, tert-butyl pyrocatechol, phenothiazine, hydroxylamines, nitro compounds, and hindered phenols. However, many of these compounds present disadvantages such as high toxicity, instability  
25 and explosion hazard under elevated temperatures, or insufficient efficacy under processing conditions (i.e., inhibitor requires oxygen to be effective). The present inventors have discovered a novel composition and method for inhibiting vinyl aromatic monomer polymerization that avoids these problems associated with known inhibitors.

The dinitrosalicylic acid, derivatives and isomers generally have the structure:



wherein  $\text{R}_1$  is H, phenyl, methyl, ethyl, n-propyl, isopropyl, n-butyl and isobutyl.

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Preferred dinitrosalicylic acid derivatives include but are not limited to 3,5-dinitrosalicylic acid (NS) and 3,5-dinitrosalicylic methyl ester (NSME).

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The dinitrosalicylic acid isomers comprise 3,5-dinitro-4-hydroxybenzoic acid and esters thereof wherein  $\text{R}_1$  in the above formula has the same designations.

20 The hydroxylamine compounds useful in this invention generally have the formula:



wherein  $\text{R}_2$  and  $\text{R}_3$  are the same or different and are hydrogen, alkyl, aryl, alkaryl, aralkyl, or hydroxyalkyl groups and preferably have about

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The composition of the present invention may be added to the vinyl aromatic monomer as either a dispersion or as a solution using a suitable liquid carrier or solvent. Any solvent that is compatible with the individual ingredients of the composition and the vinyl aromatic monomer  
5 may be employed.

Accordingly, it is possible therefore to produce a more effective vinyl aromatic monomer polymerization inhibition treatment than is obtainable by the use of either ingredient alone when measured at comparable treatment levels. This enhanced activity, particularly at temperatures of 110°C or higher, allows for the concentration of both ingredients  
10 to be lowered and the total quantity of polymerization inhibitor required, particularly at higher processing temperatures, to be reduced.

## 15 MODES FOR CARRYING OUT THE INVENTION

This invention will now be further described with reference to a number of specific examples which are to be regarded solely as illustrative and not as restricting the scope of the invention.

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### Examples

In order to evaluate the improved polymerization inhibition of the inventive composition and to demonstrate the enhanced activity of the  
25 composition, polymerization testing was performed.

of either ingredient individually. As disclosed in U.S. 4,389,285, 3,5-dinitrosalicylic acid (NS) inhibits the polymerization of styrene. Here the inventive composition provides enhanced activity when compared to the NS alone.

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Freshly distilled uninhibited styrene (100 mL) was placed in a three-necked flask fitted with a condenser, a bubbler, and a rubber septum. The inhibitor treatment was added and argon was bubbled through the liquid at 15 mL/min with stirring from a magnetic stirrer. After 20 minutes the flask was immersed in a heated oil-bath. Argon bubbling was continued throughout the test. Samples were taken every half-hour. The amount of polystyrene formed was determined by methanol precipitation. Results of this testing are presented in Table II.

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**TABLE II**

Styrene Polymerization Test

Distilled, uninhibited styrene at 120°C

Treatment: 3,5-dinitrosalicylic acid methyl ester/bis-(hydroxypropyl) hydroxylamine (300/300 ppm)

20	<u>Time (min.)</u>	<u>% Polymer formed</u>
	30	0.09
	60	0.26
	90	0.57
	120	0.91
25	150	1.32
	180	1.78

The results of this testing demonstrate that the inventive composition is effective at inhibiting the polymerization of styrene in an oxygen-free system and at elevated processing temperatures.

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Having thus described the invention, what we claim is:

1. A composition comprising a dinitrosalicylic acid, derivative or isomer thereof and a hydroxylamine compound.

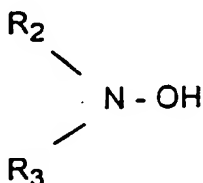
2. The composition as claimed in claim 1 characterized in that the dinitrosalicylic acid, derivative or isomer thereof has the formula:



10 wherein  $R_1$  is H, phenyl, methyl, ethyl, n-propyl, isopropyl, n-butyl and isobutyl.

3. The composition as claimed in claim 1 or 2 characterized in that the dinitrosalicylic acid derivative is selected from the group consisting of 3,5-dinitrosalicylic acid and 3,5-dinitrosalicylic methyl ester.

4. The composition as claimed in any one of the previous claims characterized in that the hydroxylamine compound has the formula:



# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US96/05531

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C07C 7/20

US CL :585/3, 4, 5

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 585/3, 4, 5

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 4,389,285 (DOUGLAS ET AL.) 21 June 1983, aBSTRACT	1-9
A	US, A, 4,439,278 (DOUGLAS ET AL.) 27 March 1984, abstract	1-9
A	US, A, 4,466,905 (BUTLER ET AL) 21 August 1984, Abstract	1-9

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	* T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
* A* document defining the general state of the art which is not considered to be of particular relevance	* X	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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